

## **APPENDIX G**

### **Partition Coefficients For Plutonium**

## Appendix G

### Partition Coefficients For Plutonium

#### G.1.0 Background

A number of studies have focussed on the adsorption behavior of plutonium on minerals, soils, and other geological materials. A review data from diverse literature sources indicated that  $K_d$  values for plutonium typically range over 4 orders of magnitude (Thibault *et al.*, 1990). Also, from these data a number of factors which influence the adsorption behavior of plutonium have been identified. These factors and their effects on plutonium adsorption on soils and sediments were used as the basis for generating a look-up table. These factors are:

- Typically, in many experiments, the oxidation state of plutonium in solution was not determined or controlled therefore it would be inappropriate to compare the  $K_d$  data obtained from different investigations.
- In natural systems with organic carbon concentrations exceeding ~10 mg/kg, plutonium exists mainly in trivalent and tetravalent redox states. If initial plutonium concentrations exceed  $\sim 10^{-7}$  M, the measured  $K_d$  values would reflect mainly precipitation reactions and not adsorption reactions.
- Adsorption data show that the presence of ligands influence plutonium adsorption onto soils. Increasing concentrations of ligands decrease plutonium adsorption.
- If no complexing ligands are present plutonium adsorption increases with increasing pH (between 5.5 and 9.0).
- Plutonium is known to adsorb onto soil components such as aluminum and iron oxides, hydroxides, oxyhydroxides, and clay minerals. However, the relationship between the amounts of these components in soils and the measured adsorption of plutonium has not been quantified.

Because plutonium in nature can exist in multiple oxidation states (III, IV, V, and VI), soil redox potential would influence the plutonium redox state and its adsorption on soils. However, our literature review found no plutonium adsorption studies which included soil redox potential as a variable. Studies conducted by Nelson *et al.* (1987) and Choppin and Morse (1987) indicated that the oxidation state of dissolved plutonium under natural conditions depended on the colloidal organic carbon content in the system. Additionally, Nelson et al (1987) also showed that plutonium precipitation occurred if the solution concentration exceeded  $10^{-7}$  M.

A number of investigators have examined potential adsorption of plutonium on minerals, soils, and other geological substrates. Earlier experiments conducted by Evans (1956), Tamura (1972), Van Dalen *et al.* (1975) showed that plutonium adsorption onto mineral surfaces was influenced significantly by the type of mineral, the pH and mineral particle size. The reported values ranged from zero for quartz (Tamura, 1972) to 4,990 ml/g for montmorillonite (Evans, 1956). [The  $K_d$  for glauconite tabulated by Evans (1956) was listed as “infinite”(certainly greater than 5,000 ml/g), because the concentration of dissolved plutonium measured in the  $K_d$  defemination was below detection.] These  $K_d$  values are only qualitative because, the initial concentrations of plutonium used in these experiments were apparently high enough to induce precipitation of plutonium solid phases therefore, the observed phenomena was likely due to mainly precipitation and not adsorption. Second, the redox status of plutonium was unknown in these experiments thus these reported  $K_d$  values cannot be  $K_d$  readily compared to values derived from other experiments.

The importance of the plutonium redox status on adsorption was demonstrated by Bondietti *et al.* (1975) who reported about 2 orders of magnitude difference in  $K_d$  values between hexavalent (250 ml/g) and tetravalent (21,000 ml/g) plutonium species adsorbing on to montmorillonite. Bondietti *et al.* (1975) also demonstrated that natural dissolved organic matter (fulvic acid) reduces plutonium from hexavalent to tetravalent state thus potentially affecting plutonium adsorption in natural systems. Some of the earlier adsorption experiments also demonstrated that complexation of plutonium by various ligands significantly influences its adsorption behavior. Increasing concentrations of acetate (Rhodes, 1957) and oxalate (Bensen, 1960) ligands resulted in decreasing adsorption of plutonium. Adsorption experiments conducted more recently (Sanchez *et al.*, 1985) indicate that increasing concentrations of carbonate ligand also depresses the plutonium adsorption on various mineral surfaces.

Even though the adsorption behavior of plutonium on soil minerals such as glauconite (Evans, 1956), montmorillonite (Billon, 1982; Bondietti *et al.*, 1975), attapulgite (Billon, 1982), and oxides, hydroxides, and oxyhydroxides (Evans, 1956; Charyulu *et al.*, 1991; Sanchez *et al.*, 1985; Tamura, 1972; Ticknor, 1993; Van Dalen *et al.*, 1975) has been studied, correlative relationships between the type and quantities of soil minerals in soils and the overall plutonium adsorption behavior of the soils have not been established.

Adsorption experiments conducted by Billon (1982) indicated  $K_d$  values for Pu(IV) ranging from about 32,000 to 320,000 ml/g (depending on pH) for bentonite or attapulgite as adsorbents. Because of relatively high initial concentrations of plutonium [ $1.7 \times 10^{-6}$  to  $4 \times 10^{-6}$  M of Pu(IV)] used in these experiments, it is likely that precipitation and not adsorption resulted in very high  $K_d$  values. Additional experiments conducted with Pu(VI) species on bentonite substrate resulted in  $K_d$  values ranging from about 100 to 63,100 ml/g when pH was varied from 3.1 to 7.52. The validity of these data are questionable because of high initial concentrations of plutonium used in these experiments may have induced precipitation of plutonium.

Experiments conducted by Ticknor (1993) showed that plutonium sorbed on goethite and hematite from slightly basic solutions [(pH: 7.5) containing high dissolved salts, but extremely low

bicarbonate concentrations ( $8.2 \times 10^{-6}$  to  $2.9 \times 10^{-4}$  M)] resulted in distribution coefficients,  $K_d$ , ranging from 170 to 1,400 ml/g. According to Pius *et al.* (1995), significant removal of Pu(IV) from solutions containing 0.1 to 1 M concentrations of sodium carbonate was observed with alumina, silica gel, and hydrous titanium oxide as substrates. These investigators also noted that the presence of carbonate lowered the sorption distribution coefficient for these adsorbents. However, even at 0.5 M carbonate, the coefficients were 60 ml/g, 1,300 ml/g, and 15,000 ml/g, respectively, for alumina, silica gel, and hydrous titanium oxide. In another study using bicarbonate solutions, the distribution coefficient for Pu(IV) sorption on alumina was lowered to about 30 ml/g at 0.5 M bicarbonate (Charyulu *et al.*, 1991). However, one should note that the initial concentrations of Pu(IV) used by these investigators ranged from  $8.4 \times 10^{-6}$  to  $4.2 \times 10^{-5}$  M, which means that the solutions were probably supersaturated with respect to  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  solid phase. Because of the experimental conditions used by Pius *et al.* (1995) and Charyulu *et al.* (1991), the principal mechanism of plutonium removal from solution could have been precipitation as easily as adsorption.

Barney *et al.* (1992) measured adsorption of plutonium from carbonate-free wastewater solutions onto commercial alumina adsorbents over a pH range of 5.5 to 9.0. Plutonium adsorption  $K_d$  values increased from about 10 ml/g at a pH of 5.5 to about 50,000 ml/g at a pH of 9.0. The slopes of the  $K_d$  compared to the pH curves were close to 1, which indicated that 1 hydrogen ion is released to the solution for each plutonium ion that is adsorbed on the alumina surface. This behavior is typical of adsorption reactions of multivalent hydrolyzable metal ions with oxide surfaces. Changing the initial concentration of plutonium from about  $10^{-9}$  to  $10^{-10}$  M did not affect the  $K_d$  values, which showed that plutonium precipitation was not significant in these tests. Also, the initial plutonium concentrations were below the measured solubility limits of plutonium hydroxide. This experiment demonstrated that in carbonate-free systems, plutonium would be adsorbed on alumina substrates.

Another study of adsorption of Pu(IV) and Pu(V) on goethite was conducted by Sanchez *et al.* (1985). The experimental conditions used by these investigators were evaluated for assessing whether the reaction being studied was indeed adsorption. The initial plutonium concentrations used in their experiments were  $10^{-10}$  and  $10^{-11}$  moles per liter. These concentrations are well below the equilibrium saturation levels for  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ . The equilibrating solutions used in these experiments contained salts such as  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaHCO}_3$  and did not contain any ionic constituents that may have potentially formed solid solution precipitates. Therefore, it is reasonably certain that the dominant reaction being studied was adsorption and not precipitation of pure or solid solution phases.

The Pu(IV) and (V) adsorption data obtained in 0.1 M  $\text{NaNO}_3$  electrolyte medium by Sanchez *et al.* (1985) indicated isotherms typical of metal and/or metal-like complex specie adsorption on substrate (Benjamin and Leckie, 1981). This indicated that Pu(IV) and Pu(V) adsorbed onto the ionized hydroxyl sites in the form of free ions and their hydrolytic species with metal ion and the metal-ion part of the complexes adsorbing onto the surface. The adsorption isotherms obtained at the higher initial concentration ( $10^{-10}$  M) of total soluble Pu(IV) and Pu(V) showed that the adsorption edges (pH value at which 50 percent adsorption occurs) increased towards a higher

pH value, which is typical of the metal-like adsorption behavior of adsorbing species (Benjamin and Leckie, 1981). These data also showed that the adsorption edges for Pu(V) was shifted about 2 pH units higher as compared to the adsorption edges observed for Pu(IV), indicating that plutonium in the higher oxidation state (pentavalent) had lower adsorbing affinity as compared with tetravalent plutonium. This difference in adsorption was attributed to the fact that Pu(V) hydrolyzes less strongly than Pu(IV),

The Pu(IV) and Pu(V) adsorption data obtained in 0.1 M NaNO<sub>3</sub> media represents conditions where only free cations and the respective hydrolytic species are the adsorbing species. Extensive experimental observations have shown that, when present, strong complexing agents have a significant effect on the metal ion adsorption (Benjamin and Leckie, 1981). This modified adsorption behavior in the presence of complex-forming ligands is characterized by Benjamin and Leckie as ligand-like adsorption. Sanchez *et al.* (1985) also conducted experiments to examine the effect of dissolved carbonate (from 10 to 1,000 meq/l) on the adsorption of Pu(IV) and Pu(V) on goethite. Their adsorption data showed that at a fixed pH value of 8.6, increasing carbonate concentration beyond 100 meq/l greatly decreased the adsorption of plutonium in both oxidation states. These data demonstrated that practically no Pu(IV) or Pu(V) adsorption occurred on goethite when the total carbonate concentration approached 1,000 meq/l (0.5 M CO<sub>3</sub>). However, data collected by Glover *et al.* (1976) showed that, at very low concentrations of dissolved carbonate (*i.e.*, 0.1-6 meq/l) typically encountered in soils, adsorption of Pu(IV) increased with increasing dissolved carbonate concentration. These results indicate that Pu(IV) in these soils may adsorb in the form of PuHCO<sub>3</sub><sup>3+</sup> species.

Such complete suppression of Pu(IV) and Pu(V) adsorption was attributed to the presence of anionic plutonium-hydroxy carbonate species in solution and to the fact that goethite at this pH contains mainly negatively charged sites that have negligible affinity to adsorb anionic species. This adsorption behavior of Pu(IV) and Pu(V) in the presence of carbonate ions that form strong hydroxy carbonate complexes is typical of ligand-like adsorption of metal ions described by Benjamin and Leckie (1981). Ligand-like adsorption is described as adsorption of a metal-ligand complex that is analogous to adsorption of the free ligand species. Also, the metal-ligand complexes may not adsorb at all if these complexes are highly stable. These data clearly demonstrate that increasing total carbonate and hydroxyl solution concentrations significantly decrease Pu(IV) and Pu(V) on iron oxyhydroxide surfaces.

Similar suppression of adsorption of higher valence state actinides in the presence of carbonate and hydroxyl ions has been observed by a number of investigators. Some of these studies include adsorption of U(VI) on goethite (Hsi and Langmuir, 1985; Koehler *et al.*, 1992; Tripathi, 1984), ferrihydrite (Payne *et al.*, 1992), and clinoptilolite (Pabalan and Turner, 1992), and Np(V) adsorption on ferrihydrite, hematite, and kaolinite (Koehler *et al.*, 1992).

Some of the early plutonium adsorption experiments on soils were conducted by Rhodes (1957) and Prout (1958). Rhodes (1957) conducted plutonium adsorption experiments using a calcareous subsurface soil from Hanford as the adsorbent. The data indicated that adsorption varied as a function of pH ranging from 18 ml/g under highly acidic conditions to >1980 ml/g at

highly alkaline conditions. These data are unreliable because initial plutonium concentration of  $6.8 \times 10^{-7}$  M used in these experiments may have resulted in precipitation of plutonium solid phases. Prout (1958) studied adsorption of plutonium in +3, +4, and +6 redox states on a Savannah River Plant soil as a function of pH. The calculated  $K_d$  ranged from  $<10$  to  $>10,000$  ml/g,  $\sim 100$  to  $\sim 10,000$  ml/g, and  $<10$  to  $\sim 3,000$  ml/g for Pu(III), Pu(IV), and Pu(VI) respectively. Maximum  $K_d$  values were observed between pH values of about 6.5 and 8.5. Because the initial concentrations of plutonium used in these experiments were about  $1 \times 10^{-6}$  M, precipitation reaction may have accounted for the observed removal of plutonium from solution phase.

Bondietti *et al.* (1975) conducted Pu(IV) adsorption studies with the clay fraction isolated from a silt loam soil as the adsorbent. The  $K_d$  values from these experiments were reported be as high as  $1.04 \times 10^6$  and  $1.68 \times 10^5$  ml/g. Experiments conducted by Dahlman et al (1976) also showed exceedingly high  $K_d$  value ( $3 \times 10^5$  ml/g) for Pu(IV) adsorption on clay fraction from a silt loam soil. In view of this anomalously high  $K_d$  value, the authors concluded that actual mechanism of plutonium removal from solution phase may have been the precipitation reaction.

Nishita *et al.* (1976) extracted plutonium from a contaminated clay loam soil with solutions ranging in pH from 1.21 to 13.25. The solution pH in these experiments were adjusted with nitric acid and sodium hydroxide. The calculated  $K_d$  from these experiments varied from 3.02 to 3,086 ml/g, with highest  $K_d$  values noted within the pH range of 4.7 to 7.1. In another set of experiments Nishita (1978) extracted plutonium from the same clay loam soil with acetate (a ligand which forms complexes with plutonium) containing extraction solutions. The pH values for these set of extractions ranged from 2.81 to 11.19. The calculated  $K_d$  values in this experiment ranged from 37 to 2,857 ml/g with highest  $K_d$  values being observed between pH values 8.6 to 9.7.

Plutonium adsorption on 14 soil samples obtained from 7 different U.S. Department of Energy (DOE) sites were studied by Glover et al (1976). Initial concentrations of plutonium in these experiments were  $10^{-8}$ ,  $10^{-7}$ , and  $10^{-6}$  M, respectively. The observed  $K_d$  values ranged from 30 to 14,000 ml/g. It is likely that removal of plutonium observed under higher initial concentrations ( $10^{-7}$ , and  $10^{-6}$  M) may have been due to precipitation reactions and not from adsorption reactions.

Rodgers (1976) conducted plutonium adsorption studies on clay and silt fractions from a glacial till soil from DOE's Mound Facility in Ohio. He noted that  $K_d$  values ranged from about 50 to 166,700 ml/g. The highest  $K_d$  values were observed between pH values of 5 to 6.

The effects of strong chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentacetic acid (DTPA) on Pu(IV) adsorption by 3 different soils were investigated by Relyea and Brown (1978). The soils used for the adsorption were a sand (Fuquay from South Carolina), a loamy sand (Burbank from Washington), and a silt loam (Muscatine from Illinois) with initial concentrations of Pu(IV) fixed at about  $5 \times 10^{-8}$  M. Without the chelating ligands, the  $K_d$  values were 316, 6,000, and 8,000 ml/g for the sand, the loamy sand, and the silt loam respectively. When  $10^{-3}$  M of EDTA was present in the matrix solution, the measured  $K_d$  values were 120, 94.5 and 338 ml/g for the sand, the loamy sand, and the silt loam respectively.

These significant reductions in adsorption were attributed to the limited affinity of Pu-EDTA complexes to adsorb onto the soil mineral surfaces. Increasing the EDTA concentration by an order of magnitude resulted in reductions in  $K_d$  values from about 1 order (for silt loam) to 2 orders (for sand) of magnitude. Using a stronger chelating agent ( $10^{-3}$  M DTPA) resulted in very low  $K_d$  values (0.12 ml/g for sand, 1.06 ml/g for loamy sand, and 0.24 ml/g for silt loam) which were about 3 to 4 orders of magnitude smaller as compared to the values from chelate-free systems. The results obtained from desorption experiments (using EDTA and DTPA ligands) showed that the  $K_d$  values were 1 to 2 orders of magnitude higher than the values calculated from adsorption experiments leading to the conclusion that some fraction of plutonium in soil was specifically adsorbed (not exchangeable). These data showed that Pu(IV) adsorption on soils would be significantly reduced if the equilibrating solutions contain strong chelating ligands, such as EDTA and DTPA.

The reduction of plutonium adsorption on soils by strong synthetic chelating agents was also confirmed by experiments conducted by Delegard *et al.* (1984). These investigators conducted tests to identify tank waste components that could significantly affect sorption of plutonium on 3 typical shallow sediments from the DOE Hanford Site. They found that sorption was decreased by the chelating agents, 0.05 M EDTA and 0.1 M HEDTA (N-2-hydroxyethylethylenediaminetriacetate) but not by low concentrations of carbonate (0.05 M). Delegard's data also showed that roughly a twofold increase in ionic strength caused an order of magnitude decrease in plutonium adsorption.

Based on an adsorption study of plutonium on basalt interbed sediments from the vicinity of Hanford site, Barney (1984) reported a  $K_d$  value of about 500 ml/g. This relatively lower  $K_d$  value may have resulted from the relatively enhanced concentration of 215 mg/l of carbonate (a complex forming ligand) which was present in the groundwater used in the experiments. Later, sorption of plutonium in +4, +5, and +6 redox states on a Hanford Site shallow sediment was studied by Barney (1992) to elucidate any differences in rate and amount of adsorption of plutonium in different redox states. The initial plutonium concentrations used in these experiments varied between about  $10^{-11}$  to  $10^{-9}$  M with synthetic ground water as a background electrolyte. The data indicated that the  $K_d$  values ranged from 2,100 to 11,600, 2,700 to 4,600, and 1,000 to 4,600 ml/g for plutonium in +4, +5, and +6 redox states, respectively. The data also indicated that Pu(V) and Pu(VI) upon adsorption was reduced to the tetravalent state. In these experiments, the  $K_d$  data obtained at lower initial concentrations ( $\sim 1 \times 10^{-11}$  M) of plutonium are reliable because the dominant plutonium removal mechanism from solution was adsorption.

Using batch equilibration techniques, Bell and Bates (1988) measured  $K_d$  values for plutonium which ranged from 32 to 7,600 ml/g. The soils used in these experiments were obtained from the Sellafield and Drigg sites in England and their texture ranged from clay to sand. Ground water spiked with about  $2.1 \times 10^{-8}$  M of plutonium was used in these adsorption experiments. The data also showed that the adsorption of plutonium on these soils varied as a function of pH, with maximum adsorption occurring at a pH value of about 6.

A number of studies indicate that  $K_d$  values for plutonium adsorption on river, oceanic, and lake sediments range from about  $1 \times 10^3$  to  $1 \times 10^6$  ml/g. Duursma and coworkers calculated that  $K_d$  for marine sediments was about  $1 \times 10^4$  ml/g (Duursma and Eisma, 1973; Duursma and Gross, 1971; Duursma and Parsi, 1974). Studies by Mo and Lowman (1975) on plutonium-contaminated calcareous sediments in aerated and anoxic seawater medium yielded  $K_d$  values from  $1.64 \times 10^4$  to  $3.85 \times 10^5$  ml/g. Based on distribution of plutonium between solution and suspended particle phases in sea water, Nelson *et al.* (1987) calculated that for plutonium in oxidized states (V, VI), the  $K_d$  was  $\sim 2.5 \times 10^3$  ml/g, and  $\sim 2.8 \times 10^6$  ml/g for plutonium in reduced states (III, IV). Based on a number of observations of lake and sea water samples, Nelson *et al.* (1987) reported that  $K_d$  values for lake particulates ranged from 3,000 to  $4 \times 10^5$  ml/g, and for oceanic particulates ranged from  $1 \times 10^5$  to  $4 \times 10^5$  ml/g.

## G.2.0 Data Set for Soils

The most detailed data set on plutonium  $K_d$  measurements were obtained by Glover *et al.* (1976). These data set were based on 17 soil samples from 9 different sites that included 7 DOE sites. The characterization of the soil included measurements of CEC, electrical conductivity, pH and soluble carbonate of the soil extracts, inorganic and organic carbon content, and the soil texture (wt.% of sand, silt, and clay content). The textures of these soils ranged from clay to fine sand. Three different initial concentrations of plutonium ( $10^{-8}$ ,  $10^{-7}$ , and  $10^{-6}$  M) were used in these experiments. This data set is the most extensive as far as the determination of a number of soil properties therefore, it can be examined for correlative relationships between  $K_d$  values and the measured soil parameters. The data set generated at initial plutonium concentrations of  $10^{-8}$  M were chosen for statistical analyses because the data sets obtained at higher initial concentrations of plutonium may have been affected by precipitation reactions (Table G.1).

## G.3.0 Approach and Regression Models

The most detailed data set on plutonium  $K_d$  measurements were obtained by Glover *et al.* (1976). This data set was based on 17 soil samples from 9 different sites that included 7 DOE sites. The characterization of the soil included measurements of CEC, electrical conductivity, pH and soluble carbonate of the soil extracts, inorganic and organic carbon content, and the soil texture (wt.% of sand, silt, and clay content). The textures of these soils ranged from clay to fine sand. Three different initial concentrations of plutonium ( $10^{-8}$ ,  $10^{-7}$ , and  $10^{-6}$  M) were used in these experiments. This data set is the most extensive as far as the determination of a number of soil properties therefore, it can be examined for correlative relationships between  $K_d$  values and the measured soil parameters. The data set generated at an initial plutonium concentration of  $10^{-8}$  M was chosen for statistical analyses because the data sets obtained at higher initial concentrations of plutonium may have been confounded by precipitation reactions

In developing regression models, initially it is assumed that all variables are influential. However, based on theoretical considerations or prior experience with similar models, one usually knows that some variables are more important than others. As a first step, all the variables are plotted in a pairwise fashion to ascertain any statistical relationship that may exist between these variables.



This is typically accomplished by the use of scatter diagrams in which the relationship of each variable with other variables is examined in a pair-wise fashion and displayed as a series of 2-dimensional graphs. This was accomplished by using the Statistica™ software. The variables graphed included the distribution coefficient ( $K_d$  in ml/g), pH, CEC (in meq/100g), electrical conductivity of soil extract (EC in mmhos/cm), dissolved carbonate concentration in soil extract (DCARB in meq/l), inorganic carbon content (IC as percent  $\text{CaCO}_3$ ), organic carbon content (OC as wt.%), and the clay content (CLAY as wt.%).

**Table G.1.** Plutonium adsorption data for soil samples. [Data taken from results reported by Glover *et al.* (1976) for measurements conducted at an initial plutonium concentrations of  $10^{-8}$  M.]

Soil Sample	K <sub>d</sub> (ml/g)	pH	CEC <sup>1</sup> (meq/100 g)	EC <sup>1</sup> (mmhos/cm)	DCARB <sup>1</sup> (meq/l)	IC % <sup>1</sup> CaCO <sub>3</sub>	OC <sup>1</sup> (% mass)	CLAY <sup>1</sup> ( % mass)
CO-A	2,200	5.7	20.0	3.6	5.97	0.4	2.4	36
CO-B	200	5.6	17.5	0.4	0.97	0.3	3.4	22
CO-C	1,900	7.9	29.6	0.4	1.98	2.4	0.7	64
ID-A	1,700	7.8	15.5	0.5	2.71	17.2	0.8	34
ID-B	320	8.3	13.8	0.8	2.51	7.9	0.2	32
ID-C	690	8.0	8.2	1.0	2.52	5.2	0.3	23
ID-D	2,100	7.5	17.5	1.2	4.90	0.0	0.1	3
WA-A	100	8.0	6.4	0.9	2.60	0.6	0.3	14
WA-B	430	8.2	5.8	0.4	2.30	0.0	0.1	14
SC	280	5.4	2.9	0.4	0.50	0.2	0.7	20
NY	810	5.4	16.0	1.2	1.40	0.0	2.7	36
NM	100	6.4	7.0	1.7	2.80	0.2	0.7	18
AR-A	710	6.2	34.4	0.5	0.10	0.9	3.2	56
AR-B	80	4.8	3.8	0.4	0.10	0.7	0.6	9
AR-C	430	2.3	16.2	0.3	0.10	0.6	2.3	37
IL	230	3.6	17.4	0.5	0.10	0.7	3.6	16
<sup>1</sup> CEC: Cation exchange capacity; EC: Electrical conductivity; DCARB: Dissolved carbonate; IC: Inorganic carbon; OC: Organic carbon; CLAY: Soil clay content.								

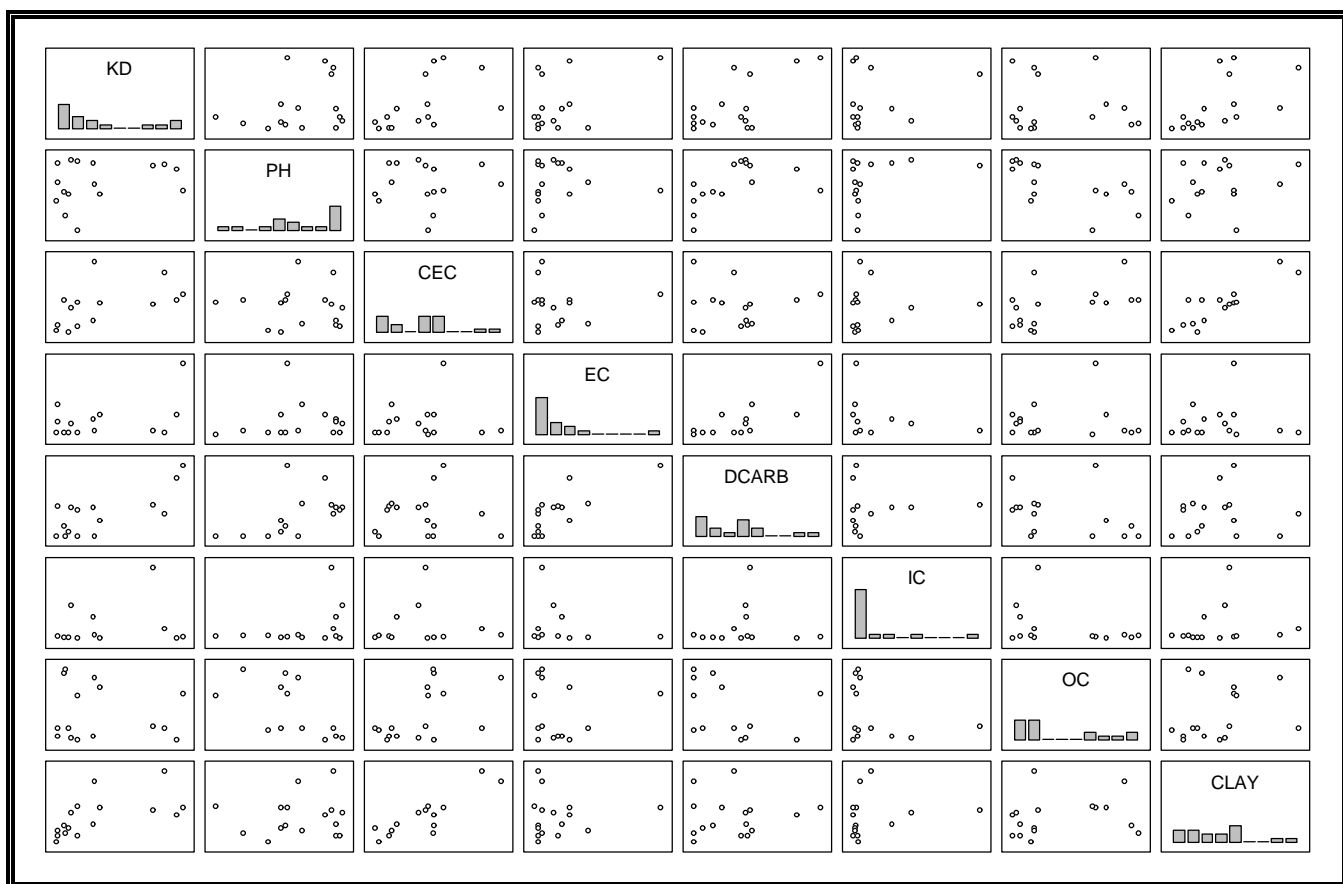
The scatterplots are typically displayed in a matrix format with columns and rows representing the dependent and independent variables respectively. For instance, the first row of plots shows the relationship between  $K_d$  as a dependent variable and other variables each in turn as selected as independent variables. Additionally, histograms displayed in each row illustrate the value distribution of each variable when it is being considered as the dependent variable.

The scatter matrix (Figure G.1) shows that regression relationships may exist between  $K_d$  and CEC, DCARB, and CLAY. Other relationships may exist between the CEC and CLAY, DCARB, and between PH, EC and DCARB. These relationships affirm that the CEC of soils depends mainly on the clay content. Similarly, the electrical conductivity of a soil solution depends on total concentrations of soluble ions and increasing dissolved carbonate concentration would contribute towards increasing EC. Also the pH of a soil solution would reflect the carbonate content of a soil with soils containing solid carbonate tending towards a pH value of ~8.3.

While a scatter diagram is a useful tool to initially assess the pairwise relationships between a number of variables, this concept cannot be extended to analyze multiple regression relationships (Montgomery and Peck, 1982). These authors point out that if there is 1 dominant regressive relationship, the corresponding scatter diagram would reveal this correlation. They also indicate however, that if several regressive relationships exist between a dependent variable and other independent variables, or when correlative relationships exist between independent variables themselves, the scatter diagrams cannot be used to assess multiple regressive relationships.

Typically, in regression model building, significant variables have to be selected out of a number of available variables. Montgomery and Peck (1982) indicate that regression model building involves 2 conflicting objectives. First, the models have to include as many independent variables as possible so that the influence of these variables on the predicted dependent variable is not ignored. Second, the regression model should include a minimum number of independent variables as possible so that the variance of predicted dependent variable is minimized.

Variable selection was conducted by using forward stepwise and backward stepwise elimination methods (Montgomery and Peck, 1982). In the forward stepwise method, each independent variable is added in a stepwise fashion until an appropriate model is obtained. The backward stepwise elimination method starts off by including all independent variables and in each step deletes (selects out) the least significant variables resulting in a final model which includes only the most influential independent variables.



**Figure G.1.** Scatter plot matrix of soil properties and the distribution coefficient ( $K_d$ ) of plutonium.

The variable selection with and without an intercept indicated that the 2 most significant variables for reliably forecasting the  $K_d$  values were the concentrations of dissolved carbonate (DCARB) and the clay content (CLAY) of soils (Table G.2). Using these 2 independent variables, several forms of polynomial regression models and a piecewise regression model with a breakpoint were generated. The results showed that the best regression model among all the models tested was the piecewise regression model. The relationship between the  $K_d$  values and the 2 independent variables (CLAY and DCARB) is shown as a 3-dimensional surface (Figure G.2). This graph illustrates that the highest  $K_d$  values are encountered under conditions of high clay content and dissolved carbonate concentrations. In contrast, the low  $K_d$  values are encountered in soils containing low clay content and low dissolved carbonate concentrations.

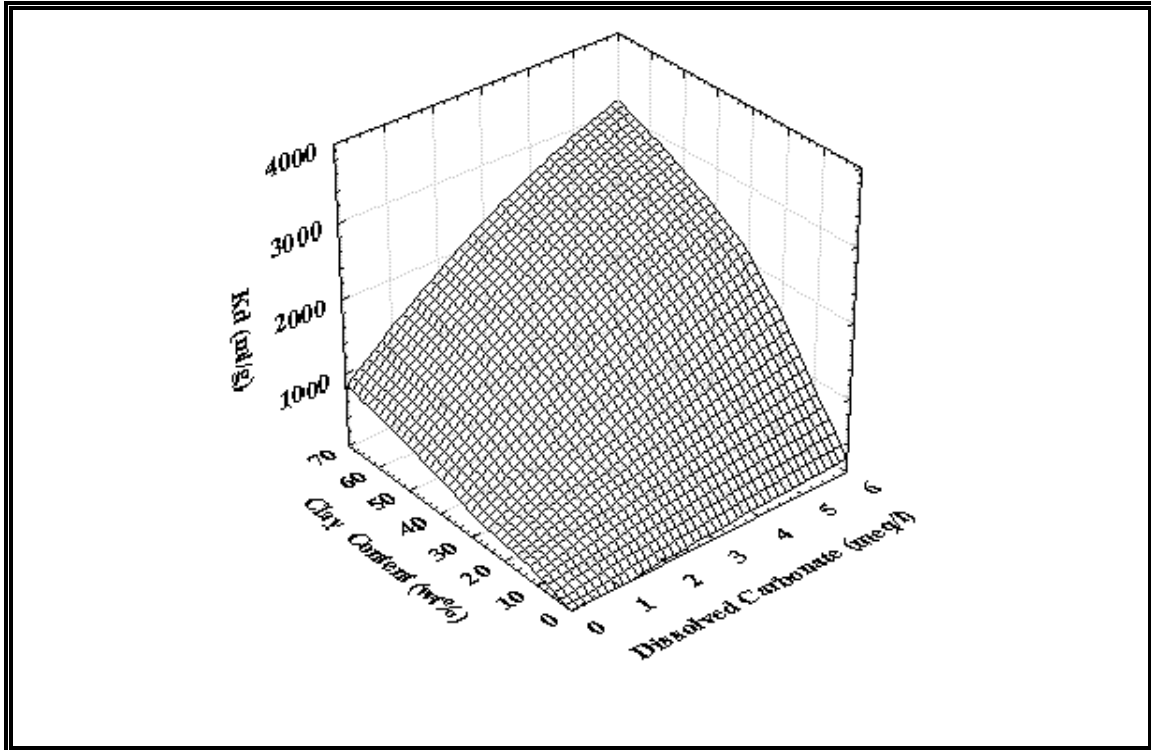
Using the piecewise regression model, a look-up table (Table G.3) was created for ranges of clay content and soluble carbonate values which are typically encountered in soils.

**Table G.2.** Regression models for plutonium adsorption.

Model Type	Forecasting Equation	R <sup>2</sup>
Linear Regression Forward Stepwise	$K_d = 284.6 (\text{DCARB}) + 27.8 (\text{CLAY}) - 594.2$	0.7305
Linear Regression Forward Stepwise	$K_d = 488.3 (\text{DCARB}) + 29.9 (\text{CLAY}) - 119.1 (\text{pH}) - 356.8 (\text{EC})$	0.8930
Linear Regression Backward Stepwise	$K_d = 284.6 (\text{DCARB}) + 27.8 (\text{CLAY}) - 594.2$	0.7305
Linear Regression Backward Stepwise	$K_d = 351.4 (\text{DCARB})$	0.7113
Piecewise Linear Regression	$K_d = 25.7 (\text{DCARB}) + 12.14 (\text{CLAY}) + 2.41$ for $K_d$ values <767.5 $K_d = 286.0 (\text{DCARB}) + 21.3 (\text{CLAY}) - 81.2$ for $K_d$ values >767.5	0.9730
Polynomial	$K_d = -156.0 (\text{DCARB}) + 15.2 (\text{CLAY}) + 16.1 (\text{DCARB})^2 - 0.04 (\text{CLAY})^2 + 11.3 (\text{DCARB})(\text{CLAY}) - 87.0$	0.9222
Polynomial	$K_d = -171.1 (\text{DCARB}) + 10.5 (\text{CLAY}) + 17.2 (\text{DCARB})^2 + 0.02 (\text{CLAY})^2 + 11.6 (\text{DCARB})(\text{CLAY})$	0.9219
Polynomial	$K_d = -106.1 (\text{DCARB}) + 11.2 (\text{CLAY}) + 12.5 (\text{DCARB})(\text{CLAY}) - 72.4$	0.9194
Polynomial	$K_d = -137.9 (\text{DCARB}) + 9.3 (\text{CLAY}) + 13.4 (\text{DCARB})(\text{CLAY})$	0.9190

**Table G.3.** Estimated range of  $K_d$  values for plutonium as a function of the soluble carbonate and soil clay content values.

$K_d$ (ml/g)	Clay Content (wt.%)								
	0 - 30			31 - 50			51 - 70		
	Soluble Carbonate (meq/l)			Soluble Carbonate (meq/l)			Soluble Carbonate (meq/l)		
	0.1 - 2	3 - 4	5 - 6	0.1 - 2	3 - 4	5 - 6	0.1 - 2	3 - 4	5 - 6
Minimum	5	80	130	380	1,440	2,010	620	1,860	2,440
Maximum	420	470	520	1,560	2,130	2,700	1,980	2,550	3,130



**Figure G.2.** Variation of  $K_d$  for plutonium as a function of clay content and dissolved carbonate concentrations.

## G.4.0 References

- Barney, G. S. 1984. "Radionuclide Sorption and Desorption Reactions with Interbed Materials from the Columbia River Basalt Formation." In *Geochemical Behavior of Radioactive Waste*, G. S. Barney, J. D. Navratil, and W. W. Schulz (eds.), pp. 1-23. American Chemical Society, Washington, D.C.
- Barney, G. S. 1992. *Adsorption of Plutonium on Shallow Sediments at the Hanford Site*, WHC-SA-1516-FP, Westinghouse Hanford Company, Richland, Washington.
- Bell, J., and T. H. Bates. 1988. "Distribution coefficients of Radionuclides between Soils and Groundwaters and their Dependence on Various test Parameters." *Science of Total Environment*, 69:297-317.
- Benjamin, M. M., and J. O. Leckie. 1981. "Conceptual Model for Metal-Ligand-Surface Interactions during Adsorption." *Environmental Science and Technology*, 15:1050-1056.
- Bensen, D. W. 1960. *Review of Soil Chemistry Research at Hanford*. HW-67201. General Electric Company, Richland, Washington.
- Billon, A. 1982. "Fixation D'elements Transuraniens a Differents Degres D'oxydation Sur Les Argiles." In *Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle*, pp. 167-176, IAEA-SM-257/32. International Atomic Energy Agency. Vienna, Austria.
- Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1975. "Interaction of Plutonium with Complexing Substances in Soils and Natural Waters." In *Transuranium Nuclides in the Environment*, pp. 273-287, IAEA-SM-199/51. International Atomic Energy Agency. Vienna.
- Charyulu, M. M., I. C. Pius, A. Kadam, M. Ray, C. K. Sivaramakrishnan, and S. K. Patil. 1991. "The Behavior of Plutonium in Aqueous Basic Media." *Journal of Radioanalytical and Nuclear Chemistry*, 152: 479-485.
- Choppin, G. R., and J. W. Morse. 1987. "Laboratory Studies of Actinides in Marine Systems." In *Environmental Research on Actinide Elements*, J. E. Pinder, J. J. Alberts, K. W. McLeod, and R. Gene Schreckhise (eds.), pp. 49-72, CONF-841142, Office of Scientific and Technical Information, U. S. Department of Energy, Washington, D.C.
- Dahlman, R. C., E. A. Bondietti, and L. D. Eyman. 1976. "Biological Pathways and Chemical Behavior of Plutonium and Other Actinides in the Environment." In *Actinides in the Environment*, A. M. Friedman (ed.), pp. 47-80. ACS Symposium Series 35, American Chemical Society, Washington, D.C.

- Delegard, C. H. , G. S. Barney, and S. A. Gallagher. 1984. "Effects of Hanford High-Level Waste Components on the Solubility and Sorption of Cobalt, Strontium, Neptunium, Plutonium, and Americium." In *Geochemical Behavior of Disposed Radioactive Waste*, G. S. Barney, J. D. Navratil, and W. W. Schulz (eds.), pp. 95-112. ACS Symposium Series 246, American Chemical Society, Washington, D.C.
- Duursma, E. K., and M. G. Gross. 1971. "Marine Sediments and Radioactivity." In *Radioactivity in the Marine Environment*, pp. 147-160, National Academy of Sciences, Washington, D.C.
- Duursma, E. K., and D. Eisma. 1973. "Theoretical, Experimental and Field Studies Concerning Reactions of Radioisotopes with Sediments and Suspended Particles of the Sea. Part C: Applications to Field Studies." *Netherlands Journal of Sea Research*, 6:265-324.
- Duursma, E. K., and P. Parsi. 1974. "Distribution Coefficients of Plutonium between Sediment and Seawater." In *Activities of the Int. Laboratory of Marine Radioactivity*, pp. 94-96, IAEA-163. International Atomic Energy Agency, Vienna, Austria.
- Evans, E. J. 1956. *Plutonium Retention in Chalk River Soil*. CRHP-660. Chalk River Laboratory, Chalk River, Canada.
- Glover, P. A., F. J. Miner, and W. O. Polzer. 1976. "Plutonium and Americium Behavior in the Soil/Water Environment. I. Sorption of Plutonium and Americium by Soils." In *Proceedings of Actinide-Sediment Reactions Working Meeting, Seattle, Washington*. pp. 225-254, BNWL-2117, Battelle Pacific Northwest Laboratories, Richland, Washington.
- Hsi, C. K. D., and D. Langmuir. 1985. "Adsorption of Uranyl onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-Binding Model." *Geochimica et Cosmochimica Acta*, 49:1931-1941.
- Koehler M., E. Wieland, and J. O. Leckie. 1992. "Metal-Ligand Interactions during Adsorption of Uranyl and Neptunyl on Oxides and Silicates." In *Proceedings of 7th International Symposium On Water-Rock Interaction -WRI7. VI: Low Temperature Environment*, Y. K. Kharaka and A. S. Maest (eds.), A. A. Balkema, Rotterdam, Netherlands.
- Mo, T., and F. G. Lowman. 1975. "Laboratory Experiments on the Transfer Dynamics of Plutonium from Marine Sediments to Seawater and to Marine Organisms." CONF-750503-5, Technical Information Center. U.S. Department of Energy, Washington, D.C.
- Montgomery, D. C., and E. A. Peck. 1982. *Introduction to Linear Regression Analysis*. John Wiley and Sons, New York, New York.



- Nelson, D. M., R. P. Larson, and W. R. Penrose. 1987. "Chemical Speciation of Plutonium in Natural Waters." In *Environmental Research on Actinide Elements*, J. E. Pinder, J. J. Alberts, K. W. McLeod, and R. Gene Schreckhise (eds.), pp. 27-48, CONF-841142, Office of Scientific and Technical Information, U.S. Department of Energy, Washington, D.C.
- Nishita, H. 1978. "Extractability of Plutonium-238 and Curium-242 from a Contaminated Soil as a Function of pH and Certain Soil Components.  $\text{CH}_3\text{COOH-NH}_4\text{OH}$  System." In *Environmental Chemistry and Cycling Process*, pp. 403-416. CONF-760429, Technical Information Center, U.S. Department of Energy, Washington, D.C.
- Nishita, H., M. Hamilton, and A. J. Steen. 1976. "Extractability of Pu-238 and Cm-242 from a Contaminated soil as a Function of pH and Certain Soil Components." *Soil Science Society of America Abstracts*, Madison, Wisconsin.
- Pabalan, R. T., and D. R. Turner. 1992. *Sorption Modeling for HLW Performance Assessment. Re. On Res. Act. For Calender Year 1991*, W. C. Patrick (ed.), pp. 8-1 to 8-66. CNWRA 91-01A. Center for Nuclear Waste Regulations and Analysis, San Antonio, Texas.
- Payne T. E., K. Sekine, J. A. Davis, and T. D. Waite. 1992. "Modeling of Radionuclide Sorption Processes in the Weathered Zone of the Koongarra Ore Body." In *Alligator Rivers Analogue Project Annual Report, 1990-1991*, P. Duerden (ed.), pp. 57-85. Australian Nuclear Science and Technical Organization, Australia.
- Pius, I. C., M. M. Charyulu, B. Venkataramani, C. K. Sivaramakrishnan, and S. K. Patil. 1995. "Studies on Sorption of Plutonium on Inorganic Ion Exchangers from Sodium Carbonate Medium." *Journal of Radioanalytical and Nuclear Chemistry Letters*, 199:1-7.
- Prout, W. E. 1958. "Adsorption of Radioactive Wastes by Savannah River Plant Soil." *Soil Science*, 13-17.
- Relyea, J. F., and D. A. Brown. 1978. "Adsorption and Diffusion of Plutonium in Soil." In *Environmental Chemistry and Cycling Process*, CONF-760429. Technical Information Center, U.S. Department of Energy, Washington, D.C.
- Rhodes, D. W. 1957. "The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil." *Soil Science Society of America Proceedings*, 21:389-392.
- Rhoades, J. D. 1996. "Salinity: electrical Conductivity and Total Dissolved Solids." In *Methods of Soil Analysis, Part 3, Chemical Methods*, J. M. Bigham (ed.), pp. 417-436, Soil Science Society of America Inc., Madison, Wisconsin.
- Richards, L. A. 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. Agricultural Handbook 60, U.S. Department of Agriculture, Washington, D.C.

- Rodgers, D. R. 1976. "Behavior of Plutonium-238 Solutions in the Soil and Hydrology System at Mound Laboratory." In *Proceedings of Actinide-sediment Reactions Working Meeting, Seattle, Washington*, pp. 291-497. BNWL-2117, Battelle Pacific Northwest Laboratories, Richland, Washington.
- Sanchez, A. L., J. W. Murray, and T. H. Sibley. 1985. "The Adsorption of Pu (IV) and (V) of Goethite." *Geochimica et Cosmochimica Acta*, 49:2297-2307.
- Sheppard, M. I., D. H. Thibault, and J. H. Mitchell. 1987. "Element Leaching and Capillary Rise in Sandy Soil Cores: Experimental Results." *Journal of Environmental Quality*, 16:273-284.
- Tamura T. 1972. "Sorption Phenomena Significant in Radioactive Waste Disposal." In *Underground Waste Management and Environmental Implications*, pp. 318-330. American Association of Petroleum Geology Memoirs 18, Tulsa, Oklahoma.
- Thibault, D. H., M. I. Sheppard, and P. A. Smith. 1990. *A Critical Compilation and Review of Default Soil Solid/Liquid Partition Coefficients,  $K_d$ , for Use in Environmental Assessments*. AECL-10125, Whiteshell Nuclear research Establishment, Pinawa, Canada.
- Ticknor, K. V. 1993. "Actinide Sorption by Fracture-Filling Minerals." *Radiochimica Acta*, 60:33-42.
- Tripathi, V. S. 1984. *Uranium (VI) Transport Modeling: Geochemical Data and Submodels*. Ph.D. Dissertation, Stanford University, Stanford, California.
- Van Dalen, A., F. DeWitte, and J. Wikstra. 1975. *Distribution Coefficients for Some Radionuclides Between Saline Water and Clays, Sandstones and Other Samples from Dutch Subsoil*, Report 75-109, Reactor Centrum, Netherlands.